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DESIGN OF NON-LINEAR OPTICAL MATERIALS BASED ON CO-ORDINATION AND ORGANOMETALLIC COMPOUNDS

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The aim of this research project was to design co-ordination and organometallic compounds which exhibit non-linear optical properties. The synthesis of pentadionato- and catecholato- complexes was achieved and their second harmonic generation properties evaluated. A related program on icosahedral carboranes has resulted in a wide range of dipolar molecules whose second harmonic generation properties have been measured both in the solid state and in solution. The latter are most promising and suggest that under the appropriate packing conditions they could show large SHG effects. Recent results in the microwave processing of materials and in the area of molecular packing are also described.

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Introduction

The primary aim of this project was to design co-ordination and organometallic compounds which might exhibit non-linear optical properties . The potential applications of co-ordination and organometallic compounds in this field had been largely ignored and it was argued that such compounds could combine the design aspects of organic conjugated molecules and the thermal and photochemical robustness of inorganic oxides such as lithium niobate. In the proposal for the supplement our research into the field of microwave syntheses and molecular packing problems were developed to justify the aquisition of dielectric measurement facilities and molecular graphics computing hardware and software.

Progress since last report

The synthesis and characterisation of metal pentadionato complexes has been completed and their second harmonic generation properties have been studied using Kurtz powder techniques. The results have been presented at a conference [1] and a full paper has been published[2].

In the area of carborane and metallocarborane chemistry the compounds have been characterised using i.r.and n.m.r. spectroscopic techniques and in many cases single crystal X-ray diffraction experiments have also been completed. The second harmonic generation properties have been measured for all the compounds given in the scheme and E-Fish measurements on some of the more promising samples have been measured in collaboration with another group. This work is currently being prepared for publication [3]. We have also synthesised a wide range of tin compounds based on catecholato- ligands. These compound are potentially chiral and also when ligand combinations with different electron donating and accepting characteristics are used they have a large dipole moment and therefore of great potential for second harmonic generation . The S.H.G. properties of these compounds have now been reported in a full paper[4].

In summary we have achieved the synthetic targets we set for the project, built the necessary measurement facilities and also made the relevant powder measurements. The compounds which we studied did not prove to have spectacular S.H.G. properties, but nontheles have contributed to a greater understanding of the phenomenon.

The application of microwave dielectric heating techniques for the synthesis of new materials has continued to be an active area of research in my group and the results have been reported in publications [5] to [10]. The grant provided for the purchase of equipment for the measurement of dielectric properties. These prooved to be most helpful in understanding "thermal runaway effects" in microwave synthese and the results have been submitted for publication.

The design of non-linear optical materials based on molecular compounds depends critically on whether the compounds crystallise in centro-symmetric or non-centrosymmetric space groups. Therefore, however much effort is placed into the design of suitable chemical chromophores for second harmonic generation the results will be negligible unless the packing problems associated with the crystallisation of the product are also addressed. Therefore, within my group we have started a major programme to tackle these molecular packing problems. This project has been assisted considerably by the hardware and software provisions provided by the grant supplement given by AFOSR in 1989. Our initial publications in this area include an analysis of the size criteria for molecular crystallisation in molecular salts [11] and the publication of procedures for calculating the volumes, surface areas and shape characteristics of molecular ions [12].

Publications

1. C. Lamberth, D.M. Murphy and D.M.P. Mingos, *Second Harmonic Generation Properties of Some Co-Ordination Compounds Based on Pentadionato-and Polyene Ligands,* Proceedings Second Symposium on Organic Materials for Non-Linear Optics, Oxford, 183-189, 1991.

2. R.C.P. Copley, C. Lamberth, J.C. Machell, D.M. Murphy H. Powell and D.M.P.Mingos, **Journal of Materials Chemistry**, 1, 583-589 (1991)

3. D.M. Murphy and D.M.P. Mingos, **Journal of Materials Chemistry**, submitted for publication..

4. C. Lamberth, J.C. Machell, D.M.P. Mingos and T.L. Stolberg, *Preparation and Second Harmonic Generation Properties of Tris(catecholato-) Complexes of Tin(IV)*, **Journal of Materials Chemistry** , **1**, 775-780 (1991).

5. D.R. Baghurst, S.R. Cooper, D.L. Greene, D.M.P. Mingos, and S.M. Reynolds, *Application of Microwave Dielectric Loss Heating Effects for the Rapid and Convenient Synthesis of Coordination Compounds*, **Polyhedron**,, **6**, 893 (1991).

6. D.M.P. Mingos and D.L. Greene, *Application of Microwave Dielectric Heating Effects for the the Rapid and Convenient Synthesis of Ruthenium(II) Polypyridyl Complexes*, **Transition Metal Chemistry**, **16**, 71 (1991).

7. D.M.P. Mingos, *Inorganic and Organometallic Principles in the Design of Multifunctional Materials*, **Material Research Society Symposium Proceedings, 175**, 40 (1990).

8. D.M.P. Mingos, *Microwave Syntheses of Materials and Their Precursors*, Ultrastructure Processing Meeting, Orlando, 1990

9. D.M.P. Mingos, *The Synthesis of New Materials and Their Precursors Using Microwave Dielectric Heating Effects*, Institute of Metals (London) Symposium on Microwave Synthesis of Materials, London, 1-16, (1991).

10. D.R. Baghurst and D.M.P. Mingos, *Application of Microwave Dielectric Heating Effects to Synthetic Problems in Chemistry*, **Chemical Society Reviews**, 20, 1 (1991).

11. D.M.P. Mingos and A.L. Rohl, *Size and Shape Characteritics of Inorganic Ions and Their Relevance to Crystallization Phenomena*, **Inorganic Chemistry, 30**, 3679 - 3671 (1991)..

12. D.M.P, Mingos and A.L. Rohl, *Size and Shape Characteristics of Inorganic Molecules and Ions and Their Relevance to Molecular Packing Problems*, **J. Chem. Soc. Dalton Transactions**, 3419 - 3425 (1991).

COMPLETED PROJECT SUMMARY

TITLE: Design of Non-Linear Optical Materials Based on Co-ordination and Organometallic Compounds

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INCLUSIVE DATES: 1st May 1988 to 31st March 1992

CONTRACT NO: AFOSR - 88 - 0141

PUBLICATIONS:

"Second Harmonic Generation Properties of Some Co-ordination Compounds Based on Pentadionato- Ligands ", J. Materials Chemistry, **1**, 583-589 (1992) with R.C.B. Copley, C. Lamberth, J.C. Machell, D.M. Murphy and H. Powell.

"Preparation and Second Harmonic Generation Properties of Tris(catecholato)tin(IV) Compounds, J. Materials Chemistry, 1,775-780 (1991) with C. Lamberth, J.C. Machell and T.L. Stolberg.

"Second Harmonic Generation Properties of Some Co-ordination Compounds Based on Pentadionato- and Polyene Ligands", Procededings of Second Symposium on Organic Materials for Non-Linear Optics", 183-189 (1991) with C. Lamberth and D.M. Murphy.

"Size and Shape Characteristics of Inorganic Molecules and Ions and Their Relevance to Molecular Packing Problems", J. Chem. Soc. Dalton Trans., 3419-3425 (1991) with A.L. Rohl.

"Size and Shape Characteristics of Inorganic Molecules and Ions and Their Relevance to Crystallization Phenomena", Inorg. Chem., **30**, 3679-3771 (1991) with A.L. Rohl.

"Synthesis of New Materials and Their Precursors Using Microwave Dielectric Heating Effects", Proceedings of Institute of Metals Symposium on the Applications of Microwaves, 1-16 (1991).

"Applications of Micowave Dielectric Heating Effects to Synthetic Problems in Chemistry", Chem. Soc. Rev., 20, 1-47 (1991) with D.R. Baghurst.

"Systematics of Electron Rich Molecules", An Econium to Linus Pauling - Molecules in Natural Science and Medicine, Ellis Horwood, 1992 with P. Lyne.

"A New Reaction Vessel for Accelerated Syntheses Using Microwave Dielectric Superheating Effects", J. Chem. Soc. Dalton Trans., 261-268 (1992) with D.R. Baghurst.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The aim of the research project was to design co-ordination and organometallic compounds that exhibit non-linear optical properties. This has been achieved in three primary areas : transition metal co-ordination compounds based on pentadionato- ligands, icosahedral carborane cage compounds and main group co-ordination compounds based on catecholato- ligands. The S.H.G. properties have been measured in the solid state and in solution and suggest that if the molecules packed non-centrosymmetrically and with the correct phase matching criteria then these compounds could show interesting S.H.G. effects.

The packing problems associated with molecular co-ordination compounds have been addressed using computational methods and some significant insights into the crystallisation preferences of co-ordination compounds have been achieved as a result of these theoretical studies.

The synthesis of solid state compounds which might exhibit interesting non-linear optical properties has been achieved using microwave dielectric techniques. Furthermore, the measurement of dielectric properties of the precursors has provided valuable backround information on the dielectric loss tangents of a wide range of organic and inorganic compounds. This information is essential for understanding dielectric heating in the solution and solid state phases.

AFOSR PROGRAM MANAGER: Dr. C. Lee